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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This research had two goals, the development of coupled cluster theory and the application of molecular electronic structure theory to the alkali dioxide molecules $LiO_2^\square$, $NaO_2^\square$, and $KO_2^\square$. The research on coupled cluster theory was successful. It was possible to take the single and double excitation coupled cluster method (CCSD) from an exotic, fringe technique to the very center of applied quantum chemistry. Critical to this remarkable transformation was the formulation of an analytic gradient method for the CCSD method. A sustained effort on the $LiO_2^\square$ and $NaO_2^\square$ molecules was begun, however, unusual difficulties (specifically symmetry-breaking) were discovered for $LiO_2^\square$. However, all these problems were eventually solved, resulting in a massive and truly definitive paper, to be submitted for publication very shortly. Work using the same methods is well underway for $NaO_2^\square$.

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Final Report

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The Coupled Cluster Method and the Properties of Energetic Materials

Henry F. Schaefer III

This research had two goals, the development of coupled cluster theory and the application of molecular electronic structure theory to the alkali dioxide molecules LiO_2, NaO_2, and KO_2. Work on the latter three molecules was undertaken based on the U. S. Army's interest in molecular aspects of the suppression of muzzle flash associated with high-performance, large caliber systems.

The research on coupled cluster theory was successful far beyond the aspirations of our initial proposal. As the list of publications shows, we were able to take the single and double excitation coupled cluster method (CCSD) from an exotic, fringe technique to the very center of applied quantum chemistry. Critical to this remarkable transformation was the formulation of an analytic gradient method for the CCSD method.

A sustained effort on the LiO_2 and NaO_2 molecules was begun during the first year of the three-year grant period. As discussed in our sixth-month progress reports, however, unusual difficulties (specifically symmetry-breaking) were discovered for LiO_2. However, all these problems were eventually solved, resulting in a massive and truly definitive paper, to be submitted for publication very shortly.

As the LiO_2 problem was in the final stages of solution and work using the same methods well underway for NaO_2, the Army Research Office notified us that they would not support this research for the third year of the three-year grant. Thus our ARO research officially ended on May 14, 1988. Scientific integrity requires that we complete the research on NaO_2, but it was not possible to begin the proposed studies of KO_2 and its reactions.

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Scientific Publications Supported by Army Research Office (ARO) Grant DAALO3-86-K-0077

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1 G. E. Scuseria, A. C. Scheiner, T. J. Lee, J. E. Rice, and H. F. Schaefer, "The Closed-Shell Coupled Cluster Single and Double Excitation (CCSD) Model for the Description of Electron Correlation. A Comparison with Configuration Interaction (CISD) Results", *J. Chem. Phys.* **86**, 2881 (1987).

2 B. H. Lengsfield, S. Havriliak, M. E. Colvin, and H. F. Schaefer, "Analytic MCSCF Infrared Intensities: Application to Formaldehyde", *Chem. Phys. Lett.* **135**, 340 (1987).

3 T. J. Lee, G. E. Scuseria, J. E. Rice, A. C. Scheiner, and H. F. Schaefer, "Comparison of Single and Double Excitation Coupled Cluster (CCSD) and Configuration Interaction (CI) Theories: Determination of Structure and Equilibrium Properties of Diatomic Molecules, *Chem. Phys. Lett.* **139**, 134 (1987).

4 G. E. Scuseria, A. C. Scheiner, J. E. Rice, T. J. Lee, and H. F. Schaefer, "Analytic Evaluation of Energy Gradients for the Single and Double Excitation Coupled Cluster (CCSD) Wavefunction: A Comparison with Configuration Interaction (CISD, CISDT, and CISDTQ) Results for the Harmonic Vibrational Frequencies, Infrared Intensities, Dipole Moment and Inversion Barier of Ammonia", *Intern. J. Quantum Chem. Symp.* **21**, 495 (1987).

5 A. C. Scheiner, G. E. Scuseria, J. E. Rice, T. J. Lee, and H. F. Schaefer, "Analytic Evaluation of Energy Gradients for the Single and Double Excitation Coupled Cluster (CCSD) Wavefunction: Theory and Application", *J. Chem. Phys.* **87**, 5361 (1987).

6 G. E. Scuseria and H. F. Schaefer, "The Optimization of Molecular Orbitals for Coupled Cluster Wavefunctions", *Chem. Phys. Lett.* **142**, 354 (1987).

7 G. E. Scuseria and H. F. Schaefer, "Equilibrium Structures and Vibrational Frequencies for Diatomic Molecules. An Assessment of the CCSDT-1 Method, Incorporating Coupled-Cluster Single, Double and Linearized Triple Excitations", *Chem. Phys. Lett.* **148**, 205 (1988).

8 W. D. Allen, D. A. Horner, R. L. DeKock, R. B. Remington, and H. F. Schaefer, "The Lithium Superoxide Radical: Symmetry Breaking Phenomena and Potential Energy Surfaces," to be submitted to J. Chem. Phys.

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